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First-principles study of the adsorption of methanol at the α-Al_2O_3(0001) surface

Øyvind Borck[1,2] **and Elsebeth Schröder**[2]

[1] Department of Physics, Norwegian University of Science and Technology, NO-7034 Trondheim, Norway
[2] Department of Applied Physics, Chalmers University of Technology, SE-41296 Göteborg, Sweden

E-mail: oyvind.borck@phys.ntnu.no

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Abstract

We present density functional theory calculations of methanol molecular adsorption at the (0001) surface of α-Al_2O_3, for methanol coverages of 1/4 to 1 monolayer (ML). Adsorption energies, adsorption-induced restructuring of the surface, and induced changes to the electronic structure are calculated. We find that methanol bonds with its O atom to Al atoms at the α-Al_2O_3(0001) surface with an adsorption energy of 1.23 eV at coverage 1/4 ML, decreasing with coverage to 1.03 eV at 1 ML coverage. From calculations of the relaxed adsorption geometry and the angular dependence of the total energy, we predict an orientation of the adsorbed methanol molecule that has the molecular COH plane tilted away from the surface normal. The adsorption of methanol significantly restructures α-Al_2O_3(0001), especially for the outermost Al layer. Upon adsorption a small charge transfer from the molecule to the substrate takes place.

1. Introduction

Understanding the surface properties of alumina (Al_2O_3) is of considerable importance for a wide variety of technological and industrial processes, ranging from catalysis to corrosion and adhesion [1, 2]. For this reason there have been a large number of experimental and theoretical studies on alumina addressing the properties of the clean α-Al_2O_3(0001) surface [3, 4], and the adsorption of various metal atoms [5] and molecules [6, 7], including water [8–10] and methanol [11–15].

Interest in the adsorption of methanol at alumina surfaces stems mainly from its relevance in heterogeneous catalysis [11–14]. Alumina in the γ-phase is catalytically active for the dehydration of alcohols [12, 16], and is used as a support for Cu- or Pd-based catalysts employed in the decomposition of methanol [17, 18]. Methanol is also used as a probe molecule for investigating the surface chemistry of alumina and other metal oxides [19, 20].

In this paper we present density functional theory (DFT) calculations of the adsorption of methanol (CH_3OH) at the α-$Al_2O_3(0001)$ surface. Our work is motivated by the wider perspective of understanding how organic polymers interact with metal oxide surfaces. This is essential for a fundamental understanding of the adhesion of organic materials, such as adhesives and paints, to these surfaces. In this perspective, methanol is representative for the hydroxyl functionality of the polymer.

On the basis of experiments it has been suggested that the molecular (non-dissociative) adsorption dominates the adsorption mechanism [11, 13, 14] when methanol is adsorbed at the Al_2O_3 surface under ultra-high vacuum (UHV) conditions. It has been proposed that methanol chemisorbs through the interaction of the methanol oxygen lone pair with substrate aluminium atoms (cations) [11, 13]. Our investigation focuses on the energetics of and the changes to the atomic geometry and electronic structure that result from the adsorption of methanol at the α-$Al_2O_3(0001)$ surface. To determine the orientation of the methanol molecule on the α-$Al_2O_3(0001)$ surface we have, in addition to a geometry optimization, calculated the dependence of the total energy on the methanol angle with the surface.

2. Computational details

Experiments [11, 13, 14] indicate that the adsorption of methanol on α-$Al_2O_3(0001)$ is dominated by chemisorption. The distance from the most active part of the molecule to the surface (in our preliminary study found to be approximately 2 Å) is such that long-range interactions, e.g., the dispersion interaction [21], are expected to not give any significant contribution to the binding. Thus we can rely on a traditional semi-local implementation of DFT, using the generalized gradient approximation (GGA) for the exchange–correlation functional.

The calculations presented here are performed using the DACAPO DFT code [22], employing the Vanderbilt ultrasoft pseudopotentials [23], and the GGA Perdew–Wang 91 (PW91) parametrization [24] of the exchange–correlation energy. For comparison a number of energies have also been calculated in the two revised Perdew–Burke–Ernzerhof GGA parametrizations revPBE by Zhang and Yang [26] and RPBE by Hammer, Hansen, and Nørskov [25]. The Kohn–Sham wavefunctions are expanded in a plane wave basis, with a 400 eV energy cut-off.

The clean α-$Al_2O_3(0001)$ surface is modelled by a slab periodically repeated in all directions, with four layers of oxygen, keeping the bottom layer of oxygen and aluminium frozen in the bulk geometry. To reduce interactions between the periodically repeated images of the slab in the [0001] direction the slabs are separated by 15 Å of vacuum. In the (1×1) surface unit cell we use a $4 \times 4 \times 1$ mesh of Monkhorst–Pack [27] special k-points to describe the Brillouin zone. Tests with larger vacuum and slab thickness, higher cut-off energy and denser k-point sampling showed negligible changes to the energies and structural parameters. To investigate how the adsorption of methanol changes with coverage, (1×1), (2×1) and (2×2) unit cells of α-$Al_2O_3(0001)$ are employed, with k-point sampling and convergence criteria appropriately modified for the two larger surface unit cells.

In our calculations we place the molecules on one side of the slab only, and allow the atoms of both the adsorbate and of the corresponding slab surface to relax. We do not include symmetry constraints in the structural optimization. The artificial electric field created by the asymmetry of the system (also for the clean but structurally relaxed surface slab) is compensated by a self-consistently determined dipole correction applied in the vacuum region [28, 29].

This dipole correction, in combination with the 15 Å vacuum region, we find is sufficient to cancel the surface dipole. The atomic positions of the surface structure and of the CH_3OH molecules are found by locally minimizing the Hellmann–Feynman forces until the remaining total force on the unconstrained atoms is less than 0.05 eV $Å^{-1}$. For the relaxation of the atomic positions a preconditioned quasi-Newton method based on the Broyden–Fletcher–Goldfarb–Shanno algorithm [30] is used.

The adsorption energy per methanol molecule is calculated from

$$E_{\mathrm{ads}} = -(E_{\mathrm{SM}} - E_{\mathrm{S}} - E_{\mathrm{M}}), \tag{1}$$

where E_{SM} is the total energy of the α-Al_2O_3 slab with adsorbed methanol, E_{S} the energy of a clean slab of α-Al_2O_3, and E_{M} the energy of an isolated methanol molecule. With this definition, a positive adsorption energy indicates stabilization. All calculations are carried out at zero temperature, and the zero-point vibration is not taken into account. Thus the adsorption energy calculated from (1) does not include contributions from entropy.

3. Results and discussion

In this section we present our results for the adsorption of CH_3OH at the α-$Al_2O_3(0001)$ surface, as well as the structure of the clean α-$Al_2O_3(0001)$ surface and the gas-phase CH_3OH. We assume that the adsorption of methanol does not change the surface termination of α-Al_2O_3 (0001). We calculate and discuss how both the relaxation of the surface atom positions and the adsorbate relaxation contribute to the adsorption energy.

3.1. The clean α-$Al_2O_3(0001)$ surface and gas phase CH_3OH

As a first step in our study, we investigate the properties of the clean α-$Al_2O_3(0001)$ surface and the free (gas phase) methanol molecule. The bulk structure of α-Al_2O_3 is rhombohedral with a $D_{3d}^6(R\bar{3}c)$ symmetry and two Al_2O_3 formula units per primitive unit cell [31]. Following the approach described in [32] and section 2 we determine the calculated (compared to experimentally determined [33]) lattice parameters $a_0 = 5.173$ Å (5.128 Å) and $\alpha = 55.28°$ (55.28°) with internal Wyckoff positions [31] of Al, respectively O, within the unit cell $w = 0.3523$ (0.3520) and $u = 0.5561$ (0.555). These values are in good agreement with the experiments by Lee and Lagerlof [33] and previous DFT calculations [4, 34]. The calculated bulk modulus $B_0 = 228.4$ GPa is smaller than the experimental value 254 GPa by 10%.

The stacking sequence of α-Al_2O_3 along the [0001] direction is R–Al–Al–O_3–R, where R represents the continuing sequence. The (0001) surfaces can be obtained by cleaving the crystal between any of these layers, i.e., three chemically distinct (0001)-plane terminations may be produced. Previous theoretical and experimental studies have shown that under UHV conditions the Al-terminated surface obtained by cleaving between two Al sub-layers is the most stable one [10, 34–37].

Figure 1 shows a schematic side and top view of the Al-terminated α-$Al_2O_3(0001)$ surface with the (1×1) surface unit cell indicated. The calculated surface relaxations for the first four layers are listed in table 1, and are in good agreement with previous calculations [4, 10, 37]. The surface Al atoms undergo large relaxations, leaving them almost coplanar with the surface O layer. The relaxations below the top layer are also significant, and show the necessity of using a relatively thick slab for a good description of the α-$Al_2O_3(0001)$ surface. The discrepancies between the theoretical and the experimental values have been attributed to the presence of hydrogen on the experimentally observed surfaces [37].

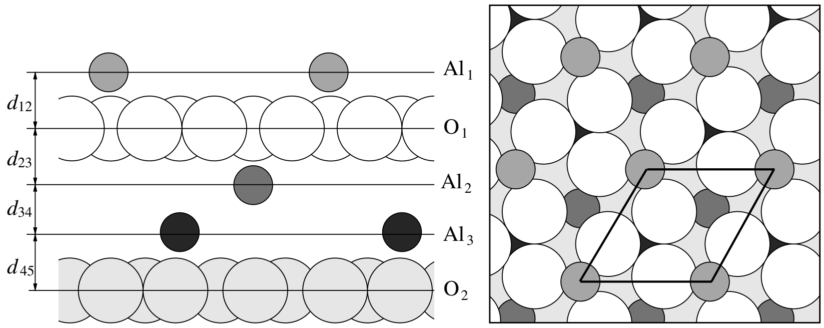

Figure 1. Schematic side and top view of the α-$Al_2O_3(0001)$ surface terminated by half a layer of aluminium. The large circles represent oxygen atoms. The (1 × 1) hexagonal surface unit cell is shown.

Table 1. Relaxations of the outermost atomic layers of the α-$Al_2O_3(0001)$ surface given in percentage deviation from the bulk structure. The PW91 parametrization of the exchange–correlation energy is used. Distances Δd_{ij} are defined in figure 1.

	Theory			Expt
	This work	[4]	[34]	[38]
$\Delta d_{12}(\%)$	−84.5	−85.5	−87.4	−51
$\Delta d_{23}(\%)$	+3.5	+3.2	+3.1	+16
$\Delta d_{34}(\%)$	−45.8	−45.4	−41.7	−29
$\Delta d_{45}(\%)$	+19.4	+19.8	+18.9	+20

In table 2 we list the geometry of the gas-phase methanol molecule as found in our calculations. We find the bond lengths and bond angles to be in excellent agreement with the experimental values of [39].

3.2. Adsorption geometries and energetics

A number of quantities may be used for describing methanol adsorption on α-$Al_2O_3(0001)$. The most immediate ones are the adsorption energy and the positional changes to the adsorbate and surface geometry upon adsorption. The adsorption energy is usually affected not only by electronic interactions in and between the adsorbate and the surface, as described for methanol on α-$Al_2O_3(0001)$ in section 3.3, but also by the energetic cost of changing the atomic geometry (deformation) of the surface and the adsorbate upon adsorption. These energy contributions to the adsorption energy are discussed below.

The adsorption of methanol was studied by initially placing the molecule with its O atom above a surface Al atom and performing a complete optimization of the adsorbate–surface geometry. We used several different initial orientations of the methanol molecule, to avoid any risk of the geometry getting stuck in a local energy minimum. The coverage dependence of methanol adsorption was studied by considering adsorption at coverages $\Theta = 1/4$ monolayers (ML), $1/2$ ML, and 1 ML. Here the coverage Θ is defined with reference to the surface aluminium layer, so that $\Theta = 1$ ML corresponds to one adsorbed molecule per surface aluminium atom. At $\Theta = 1/4$ ML the closest distance between any two atoms of neighbouring methanol molecules is 7.4 Å, sufficiently far apart for the molecules to be considered 'isolated' if any indirect interaction through the surface is neglected.

We tested whether our 15 Å vacuum region and the dipole correction applied are sufficient to overcome the effect of the surface dipole at the bottom of the slab (the bulk-truncated frozen

Table 2. Adsorption energies and selected structural data for methanol adsorbed at the α-$Al_2O_3(0001)$ surface at three different coverages. Some of the structural parameters are depicted in figure 2. The parameter $r_{\mathrm{Al-O_{ads}}}$ is the bond length between the methanol O and the nearest surface Al, h is the height of Al bounded to a methanol molecule above the average position of the layer of top O atoms, and $r_{\mathrm{H-O_s}}$ is the shortest distance between the H of the molecule OH group and an O atom at the surface. ϕ_{CO} is the tilt angle of the C–O axis away from the surface normal, and ϕ_{COH} is the tilt angle of the COH plane with respect to the surface plane. All calculations were carried out in the PW91 parametrization of the exchange–correlation functional unless explicitly noted.

	Expt [39]	Theory			
Θ (ML)	Free	Free	1/4	1/2	1
Internal geometry of the methanol molecule					
$r_{\mathrm{C-O}}$ (Å)	1.429	1.43	1.45	1.45	1.44
$r_{\mathrm{O-H}}$ (Å)	0.975	0.98	1.00	1.00	1.02
$r_{\mathrm{C-H}}$ (Å)	1.098	1.10	1.10	1.09	1.10
∠COH (deg)	107.6	109	110	110	111
∠OCH (deg)	—	112	110	109	110
	—	112	109	109	109
	—	107	107	107	108
Geometry of the adsorption bonds					
h (Å)	—	0.13	0.43	0.42	0.32
$r_{\mathrm{Al-Oads}}$ (Å)	—	—	1.93	1.95	2.00
$r_{\mathrm{H-Os}}$ (Å)	—	—	2.03	1.91	1.77
ϕ_{CO} (deg)	—	—	57	57	57
ϕ_{COH} (deg)	—	—	34	36	39
Adsorption energy contributions					
E_{ads} (eV)	—	—	1.23	1.16	1.03
Methanol deform. (eV)	—	—	0.04	0.03	0.03
Surface deform. (eV)	—	—	0.29	0.29	0.15
E_{ads} surf. undeform. (eV)	—	—	0.85	0.86	0.87
E_{ads} (RPBE) (eV)	—	—	0.97	0.88	0.71
E_{ads} (revPBE) (eV)	—	—	0.97	0.88	0.70

surface). We found that with methanol adsorbed on the top of the slab, the adsorption energy only changes by 0.009 eV when instead using a slab with the bottom of the slab in the relaxed geometry. Having both sides of the slab in the relaxed structure requires a thicker slab for convergence in number of atomic layers. We thus for all further calculations keep the bottom of the slab in the bulk-truncated structure.

Figure 2 shows a schematic top and side view of the optimum adsorption geometry found in our calculations, and in table 2 the calculated adsorption energies and selected bond lengths and angles are listed.

We find that methanol adsorbs with its O atom (denoted O_{ads}) approximately on top of a surface Al atom, with the methyl group pointing away from the surface and the OH group pointing toward one of the three equivalent surface O atoms (denoted O_s) around the Al adsorption site. The methanol C–O axis is tilted away from the surface normal by $\phi_{\mathrm{CO}} = 57°$ at the coverages considered here. Experiments indicate that the C–O axis is indeed tilted away from the surface normal on Al_2O_3 [11, 14]; however, to the best of our knowledge, no detailed experimental structural data are yet available for this system.

The methanol molecule is laterally displaced from the precise Al atop site by ~0.6 Å towards the surface O_s atom; see figure 2. The OH group is oriented towards O_s, and the

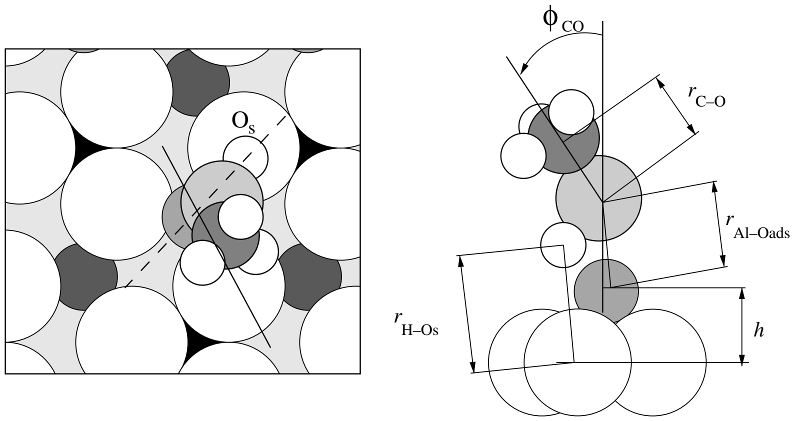

Figure 2. Schematic top (left panel) and side view (right panel) of the stable configuration of the CH_3OH molecule on the α-$Al_2O_3(0001)$ surface. In the left panel, the full and dashed lines indicate the positions of the planes used for the cross sections of the electron density difference displayed in figure 4. In the right panel some of the structural parameters of table 2 are defined.

O_{ads}–H bond length is elongated by 0.02–0.04 Å compared to the gas phase value (table 2). This suggests that the H–O_s interaction is significant. Further evidence of this interaction is that the H–O_s distances, 1.77–2.03 Å, are significantly shorter than the sum of the respective van der Waals radii (2.72 Å, [40]).

Apart from the above-mentioned elongation of the molecular O_{ads}–H bond, the geometry of the molecule is only moderately affected by the adsorption. The COH angle opens up compared to the gas phase value by 1°–2°, and the C–O_{ads} bond lengths are increased, but by no more than 0.02 Å. There are no changes to the C–H bond lengths, but the HCH angles open up by $\sim 2°$.

As the coverage is increased from $\Theta = 1/4$ ML to 1 ML we find a slight change in the geometry of the adsorbed methanol atom. The tilt angle ϕ_{COH} between the molecular dipole plane (the COH plane) and the surface plane changes from 34° to 39°, and the Al–O_{ads} distance is elongated from 1.93 to 2.00 Å. These bond lengths are comparable to the two Al–O bonds in the α-Al_2O_3 bulk crystal, in our calculations 1.87 and 1.99 Å, and to Al–O_{ads} distances reported in DFT studies of adsorption of water molecules onto the α-$Al_2O_3(0001)$ surface [8, 10].

Whereas the geometrical changes to the methanol molecule are small, adsorption of methanol results in significant surface relaxations in α-$Al_2O_3(0001)$. The most prominent change is the displacement of the Al atoms along the surface normal. The Al atoms directly beneath CH_3OH relax outwards by 0.19–0.30 Å. At $\Theta < 1$ ML, the surface Al atoms *without* methanol bounded to them descend into the outermost O layer, so that at $\Theta = 1/4$ ML they are coplanar with the O layer (less than 0.05 Å above the O layer) and at $\Theta = 1/2$ ML they are positioned slightly below the O layer (−0.14 Å). Similar relaxation effects have been reported in theoretical studies of the adsorption of water [10, 8] and HCl [7] at the α-$Al_2O_3(0001)$ surface.

To study the sensitivity of the adsorption geometry to positional perturbations (e.g., at finite temperatures) additional static calculations were carried out, changing the orientation of the molecule with the O_{ads} position kept fixed. In the left panel of figure 3 we plot the variation of the adsorption energy as a function of the C–O axis tilt angle, ϕ_{CO}. A tilt angle of 0° corresponds to the C–O axis being parallel to the surface normal. The plot has a minimum at $\phi_{CO} \approx 60°$, confirming the result of our geometry optimization.

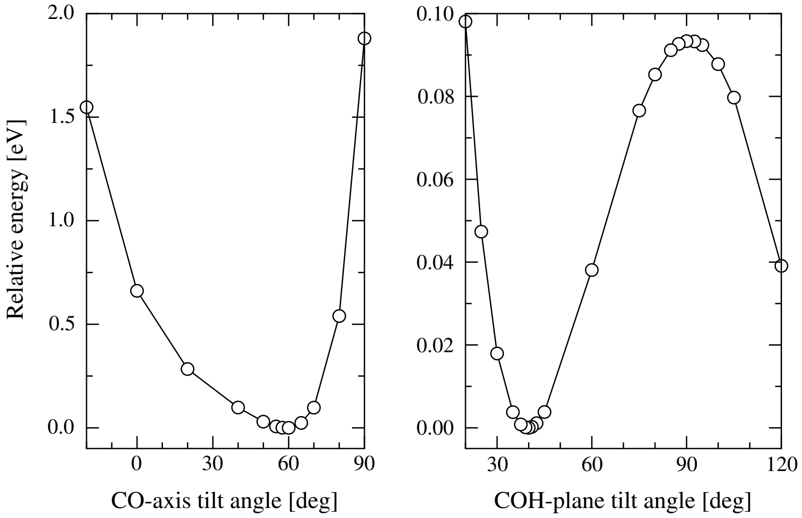

Figure 3. The variation of the total energy for CH_3OH on α-$Al_2O_3(0001)$ as a function of the tilt angle of the C–O axis (left panel) and the COH plane (right panel). In the left panel a tilt angle of 0° corresponds to the C–O axis parallel to the surface normal. In the right panel a tilt angle of 90° corresponds to upright CH_3OH with the O end down. The calculations were carried out at $\Theta = 1$ ML.

We found that changing the direction of the C–O axis even slightly causes a huge energetic cost. Exploring the variation of the adsorption energy as the COH-plane tilt angle (ϕ_{COH}) is changed, we therefore kept $\phi_{CO} = 60°$ fixed. In this case $\phi_{COH} = 0°$ corresponds to the COH plane parallel to the surface, while at $\phi_{COH} = 90°$ the COH plane is in the plane of the surface normal. The results, displayed in the right panel of figure 3, show an energy minimum at about $\phi_{COH} \approx 40°$, consistent with our optimized adsorption geometry. However, the energy variation with ϕ_{COH} is much smaller than the dependence on ϕ_{CO}. This agrees with our finding (in table 2) that ϕ_{COH} does change, although only by a few degrees, as the methanol coverage is increased. We note that at $\phi_{COH} = 90°$ the energy is at its maximum, reflecting the fact that upright methanol molecules are not only energetically unfavourable, compared to the 40° tilt, but also unstable.

The energetic gain of adsorbing one methanol molecule, relative to the clean α-$Al_2O_3(0001)$ and the gas-phase methanol molecule, is approximately 1 eV per molecule (table 2). Methanol is thus rather strongly bound to the surface. As noted above, methanol adsorption induces significant surface deformations (whereas the deformation of the methanol molecule is small). The net adsorption energy is thus composed of both an energetic cost of deforming the surface (and a small cost of deforming the molecule), as well as a gain from the interaction in the electronic charge density, resulting in a net energy gain.

We calculated the energetic cost of the surface and molecule deformation (table 2) and found the cost of surface deformations to be 0.29 eV per molecule at $\Theta < 1$. This is about one-quarter of the net adsorption energy, thus the surface deformation is a very important part of the adsorption energetics. For denser coverage ($\Theta = 1$) the surface deformation is less, and the energetic cost at 0.15 eV per molecule is not quite as important, although still not negligible. The deformation of methanol has a smaller energy cost of only 0.03–0.04 eV per molecule and is at $\Theta < 1$ negligible compared to the surface deformation cost.

A different way of estimating the importance of surface relaxations is to calculate the adsorption energy of methanol adsorbed at a frozen surface, i.e., with all surface atoms frozen in the clean-slab positions. At $\Theta = 1/4$ ML we calculated a (frozen surface) adsorption energy of 0.85 eV/molecule, which is a reduction of 0.38 eV/molecule compared to the situation when surface relaxations are included. On the *frozen* surface the adsorption energies at $\Theta = 1$ ML and 1/4 ML are almost equivalent, differing by only 0.02 eV/molecule.

The adsorption energy (on the deformed surface) decreases with coverage from 1.23 eV/molecule at $\Theta = 1/4$ ML to 1.03 eV/molecule at $\Theta = 1$ ML, indicating repulsive adsorbate–adsorbate interactions on the surface. Since methanol adsorption induces significant surface deformations the repulsion may be caused by indirect adsorbate interactions mediated by the local deformation of the surface [41]. This is strongly supported by the fact that the frozen-surface adsorption energies do not change with coverage.

The molecules adsorbed on the surface may interact with neighbouring adsorbed molecules indirectly, through the deformation of the surface as discussed above, but also more directly, e.g., by mutually imposed static changes to the electron structure or by dispersive interactions. Below we discuss contributions from these short- and long-range direct interactions.

In the 2×2 structure the adsorbates are too far apart (>7 Å) for the direct interactions to have any significant influence on the adsorbate repulsion, compared to the size of the indirect interactions (0.29 eV cost per adsorbed molecule, table 2). This includes the long-range, dispersive interactions. In the 2×2 structure direct interactions can thus be ignored.

In the denser 1×1 and 1×2 structures the shortest distance between atoms in two neighbouring molecules is 2.7 Å. Thus direct interaction could possibly influence the adsorbate repulsion. The *short-ranged* part of the direct interaction between these molecules (as calculated within the GGA approximation) shows an attraction of 0.03 eV per pair interaction. In the 1×1 structure with six nearest neighbours per adsorbate the short-range part of the direct interaction thus provides a gain in adsorption energy of approximately 0.09 eV per adsorbate, compared to that of the 2×2 structure or even less dense structures. In the 1×2 structure, with only two nearest neighbours per adsorbate, this gain is merely 0.03 eV per adsorbate. Although in general the *long-range* interactions may also become important at the 2.7 Å distance, already the surface relaxations contribute an energy repulsion much larger than any realistic value of the (direct) long-range interaction between the methanol molecules. We therefore neglect any dispersive direct interaction between the molecules also in the 1×1 and 1×2 structures.

The deformation of the surface at adsorption carries a significant energy cost, at any coverage. For adsorption to still be favourable over no adsorption the energy gain due to changes in the electron structure must more than overcome this deformation cost. From the net adsorption energy E_{ads} and the costs of deforming the surface and the methanol molecule (table 2) the gross interface electron-density-related energy gain E_{gross} is calculated to be 1.56, 1.48, and 1.21 eV per molecule for coverages 1/4, 1/2, and 1 ML. Although the dense 1×1 structure is the structure most favoured both by the direct adsorbate–adsorbate interaction (largest gain in adsorption energy), and by the indirect interaction through the deformation of the surface (smallest cost of deformation), this is not sufficient to overcome the E_{gross} advantage of the 2×2 structure.

All adsorption energy and geometry calculations mentioned above were found by using the PW91 approximation for the exchange–correlation energy. To test our results we also carried out some of the calculations in the revPBE and RPBE approximation (table 2). Although all values of E_{ads} are found to be smaller using revPBE and RPBE the changes in magnitude with coverage are very close to those of the PW91 calculations. Thus the calculations using the revPBE or RPBE approximation support our finding that on α-Al_2O_3(0001) methanol adsorbs in a 2×2 structure rather than in the denser 1×2 or 1×1 structures. A similar decrease in adsorption energy going from the PW91 to the revPBE and RPBE approximations is also seen for O, CO, and NO adsorption on late transition metal surfaces [25].

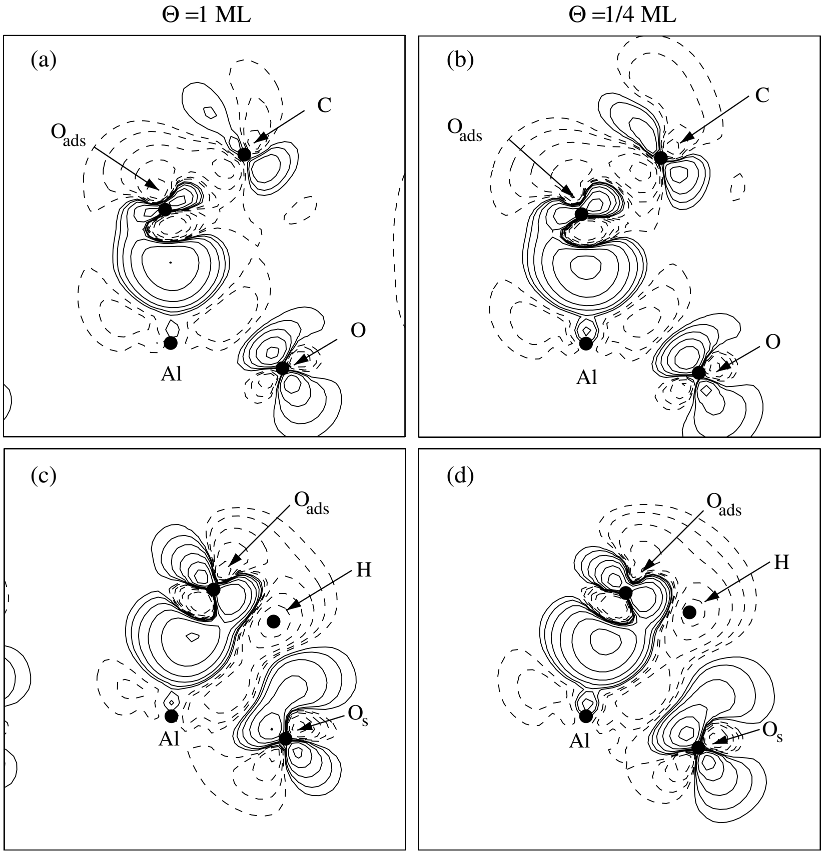

Figure 4. Contour plots of the electron density difference $\Delta n(\mathbf{r})$. Panels (a) and (b) show a cut through a plane containing one surface Al and O atom, and the methanol O and C atoms. Panels (c) and (d) show a cut through the plane containing one surface Al and the O_s atom, and the methanol O and H atoms, where the H atom is the one belonging to the methanol OH-group. Solid (dashed) lines indicate gain (loss) of electron density. The contours are drawn at densities $\Delta n = \pm 0.005 \times 2^k$ e Å^{-3} for $k = 0, 1, 2, 3, 4, 5$.

3.3. Adsorbate-induced changes to the electronic structure

Insight into the nature of the bonding of methanol at the α-Al_2O_3 is gained from the change in the electron density distribution as a result of the adsorbate bonding. To this end, we have calculated the electron density difference, $\Delta n(\mathbf{r})$, defined by

$$\Delta n(\mathbf{r}) = n^{\mathrm{SM}}(\mathbf{r}) - n^{\mathrm{S}}(\mathbf{r}) - n^{\mathrm{M}}(\mathbf{r}). \tag{2}$$

Here, n^{SM} is the electron density of the adsorption system, and n^{S} and n^{M} the electron density of the clean slab and a free methanol layer, respectively. The atomic geometry of the relaxed adsorption system is kept in the calculation of n^{S} and n^{M}. The quantity Δn gives a measure of the charge rearrangements induced by the adsorption, with a positive (negative) value in regions with a gain (loss) in electron density.

In figure 4 we display contour plots of cross sections of Δn. We chose two different planes for these cross sections. Left panels show Δn at $\Theta = 1$ ML, right panels $\Theta = 1/4$ ML. Figures 4(a) and (b) show a cut through the plane containing the O_{ads} and C atoms of the molecule, the Al bound to O_{ads}, and one of the surface O atoms. In figures 4(c) and (d) the

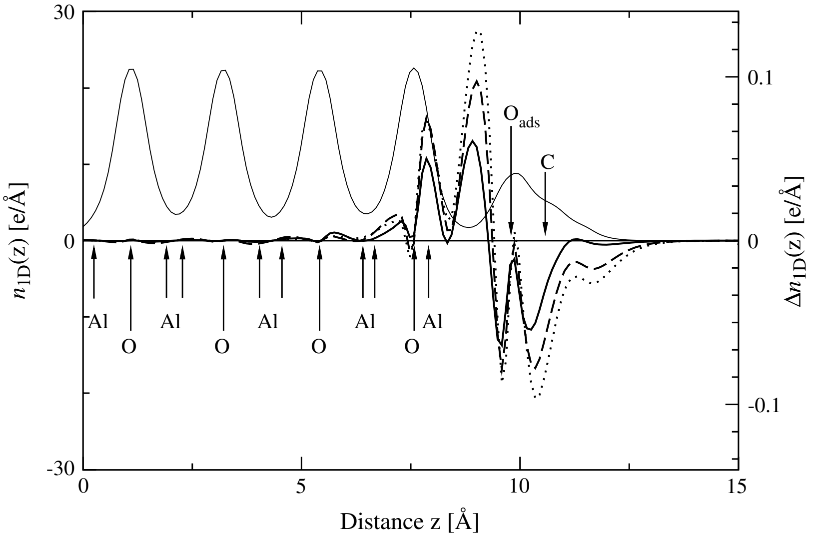

Figure 5. Profiles of the total electron density, n_{1D}, (at $\Theta = 1$ ML, thin solid line) and electron density difference, Δn_{1D}, across the slab. The thick dotted, dashed and solid lines represent Δn_{1D} at coverage $\Theta = 1/4$, $1/2$, and 1 ML, respectively. The zero-point of the z-axis is arbitrarily set to the bottom of the slab used. The positions of the Al and O layers of the slab and the O_{ads} and C atoms of the methanol molecule are indicated.

cut is through the plane defined by the methanol O_{ads} and H atoms, the Al bound to O_{ads}, and one of the surface O atoms. We first of all note the similarity in the shape of the difference densities for coverages $\Theta = 1$ ML and $1/4$ ML. This suggests that the nature of the bonding is similar.

Adsorption of methanol mainly perturbs the part of the electron density related to the topmost layer of the slab. This can most easily be seen from the electron density difference profile, $\Delta n_{1D}(z)$, displayed in figure 5 for $\Theta = 1$ ML. The figure shows that there is a net gain in electron density in the surface and interface region, and a loss of electron density in the region associated with the molecule. Thus, a small charge transfer from the molecule to the surface takes place at the adsorption (for $\Theta = 1$ ML the transfer is $\sim 0.04|e|$ as estimated by integrating $\Delta n_{1D}(z)$ in figure 5 up to its minimum above the top Al atom). The plots of $\Delta n_{1D}(z)$ for $\Theta = 1/4$, $1/2$, and 1 ML are similar in shape. Each curve represents the electron density change on one methanol molecule. We see that at low coverage ($\Theta = 1/4$ ML) the redistribution of charge over the molecule is more pronounced than at higher coverages. This is consistent with the findings in figure 4.

Returning to the cross section plots of Δn in figures 4(a)–(d) we see that the electron density gain in the interface region, seen in figure 5, is the result of a pronounced accumulation of electron density in the region between the O_{ads} and Al atoms. The accumulated electron density mainly comes from the region close to the O_{ads} atom of the methanol molecule. This redistribution of electrons is suggestive of the formation of a donor–acceptor bond, where the methanol O lone pair donates electron density to the acceptor Al [1].

In the surface region, the most prominent change in the electron density is a redistribution of electron density around the surface O atoms. This is clearly a repolarization in response to the adsorption. There is a depletion of electron density in the region between the surface O atoms and the O_{ads} atom, indicating an O–O_{ads} repulsive interaction. The decreased electron density at the H atom, as seen in figures 4(c) and (d), is consistent with the elongation of the O_{ads}–H bond, and gives further evidence that the H–O_s bond contributes to the bonding of methanol at the α-$Al_2O_3(0001)$ surface.

The redistribution of the electron density may be quantified by assigning charge to the individual atoms according to the Bader space-partitioning scheme [42]. The analysis shows that upon adsorption the surface O atom closest to the hydroxyl H atom loses 0.04–0.06 electrons compared to the same atom in the clean α-$Al_2O_3(0001)$, with the largest loss at occurring at $\Theta = 1$ ML. The analysis also shows that there is no such loss when simply deforming the surface to its adsorption geometry without adding the molecule; the actual adsorption of methanol is essential for the change in assigned charge to this surface O atom. In contrast, the change in charge is insignificant at the Al atom directly beneath the molecule, both after obtaining the adsorption geometry and after adsorbing the methanol molecule.

As mentioned in the previous section, the gross interface electron-density-related energy gain E_{gross} is higher for $\Theta = 1/4$ ML than for $\Theta = 1$ ML. This is consistent with the somewhat larger magnitude of the induced density for $\Theta = 1/4$ ML compared to $\Theta = 1$ ML, seen in figure 4.

4. Summary and conclusions

We have applied first-principles density-functional theory calculations to study the adsorption of methanol on α-$Al_2O_3(0001)$ at coverages $\Theta = 1/4$ ML, $\Theta = 1/2$ ML and 1 ML.

We find that methanol bonds to the surface Al atoms via the methanol O atom. Plots of the electron density difference, figure 4, indicate that the adsorption mechanism is a donor–acceptor interaction, where the methanol lone pair orbital donates electron density to the surface Al cations. This is the expected adsorption mechanism for alcohols at wide bandgap insulator surfaces, such as α-$Al_2O_3(0001)$ [1].

In addition to this mechanism, we find evidence that the interaction of the hydroxyl hydrogen with a surface oxygen atom also contributes to the bonding. The methanol molecule is preferentially oriented with the C–O axis tilted away from the surface normal, and the OH group oriented toward one of the surface O atoms. The elongated O_{ads}–H bonds, the short H–O_s nearest-nearest-neighbour distance, table 2, and the depletion of electron density around the H atom, figure 4, is evidence of a significant H–O_s interaction. A similar adsorption mechanism has been proposed for adsorption of methanol on NiO_x/Ni{110} [43].

The adsorption of methanol results in a significant relaxation of the surface structure. In particular, the surface Al atoms are displaced along the surface normal so that the Al bounded to methanol molecules increase their distance to the oxygen layer, and the Al not bounded to methanol descend into the topmost O layer. Our calculations show the importance of taking surface relaxation into account: At $\Theta = 1/4$ ML about 30% of the adsorption energy can be attributed to the relaxation effects. The surface deformation results in repulsive adsorbate interactions at the coverages considered here, so that the adsorption energy decreases from $E_{ads} = 1.23$ eV/molecule at $\Theta = 1/4$ ML to $E_{ads} = 1.03$ eV/molecule at $\Theta = 1$ ML.

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